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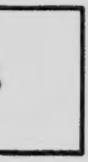

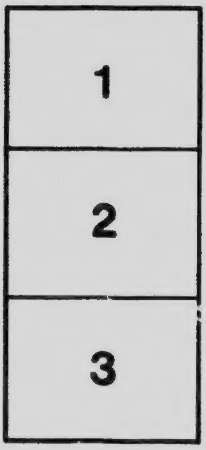

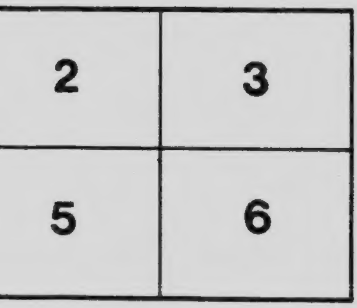

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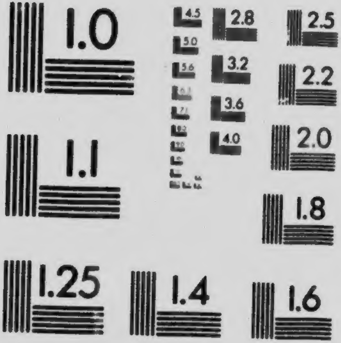

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 81: THE "MELTING-POINT" OF HYDRATED SODIUM ACETATE, BY W. F. GREEN

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THE "MELTING-POINT" OF HYDRATED SODIUM ACETATE: SOLUBILITY CURVES

BY W. F. GREEN

In the preceding paper Professor Lash Miller has shown that the composition of the crystals formed by "melting" sodium acetate trihydrate may be ascertained by means of dilatometer measurements, without isolating the crystals from the solution; the following experiments were undertaken to obtain evidence in confirmation of the result there arrived at—*viz*: that "Jeannel's leaflets" are anhydrous sodium acetate.

Isolation of the leaflets

The first attempts were made by centrifuging the mixture of leaflets and (supersaturated) mother-liquor;[1] the crystals left behind all proved to contain water (Table I,*a*), in one case more than the least found by Zettnow. That this water was due to residual solution—partly, at all events—was shown by dissolving a little rosaniline acetate in the melt; after cooling and centrifuging, the inner layers of crystals were quite colorless; but those next the cork were strongly tinged with red, showing how difficult it is to remove the viscous mother-liquor, and readily explaining the large percentage of water left in Zettnow's preparations, which were dried merely by draining in the cold.

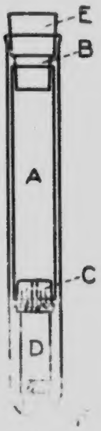

Fig. 1

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[1] The apparatus employed is represented in Fig. 1, it was designed to prevent access of dust to the supersaturated solution. The inner tube *A* was filled with the trihydrate and closed at the ends with the corks *b* and *c*, of which *c* was perforated and covered with hardened filter paper. The whole was then inserted in the outer tube, which contained a short piece of thick glass tubing *D*, provided with a perforated rubber stopper, the outer tube was then corked, *E*, and left standing, *E* down, in a steam bath until the acetate was melted. After cooling, the apparatus was placed in the centrifuge, *D* outwards, and the mother-liquor separated from the crystals which remained inside *A*.

A hundred grams of the hydrated acetate was then melted in a cylindrical tap funnel, the mouth of which was closed with a plug of cotton wool. After cooling to 15° the stem was filled with water to prevent the entrance of "germs," and connected with a vacuum pump; in this way most of the liquid was removed. The crystals were then drained for some hours in a steam bath at 95° the tap of the funnel being left open, and finally as much as possible of the remaining mother liquor was pumped off hot. On cooling, the upper part of the funnel was found to be filled with a white crust, and the bottom with moist crystals (Table I,*c*), but the crystals in the middle of the funnel retained their form and were transparent, bright and sharp, showing conclusively that they had suffered no change by being heated to 95°, but were identical with the "leaflets" deposited at 15°. Analysis showed them to be anhydrous (Table I,*b*).

Prepared in this manner, the crystals form either thin plates or long thin needles;[1] their melting-point[2] was identical with that of a sample of anhydrous acetate prepared by dehydrating the trihydrate and melting the salt so obtained; both melted at 322° to 324° uncorr.; Schaffgotsch[3] gives 319° as the melting-point of $C_2H_3O_2Na$.

Solubility determinations

Solubility of the Anhydrous Salt.—For temperatures above 58° the determinations were made in an open test tube of 100 cc capacity, in which the crystals prepared as just described were stirred with water by a strip of window glass bent into a spiral and fused to a glass rod. The apparatus stood in a thermostat, except for the determination at 123° when the contents of the tube were boiled over a Bunsen flame.

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[1] According to Haushoffer (Zeit. f. Krystallogr., **4**, 572 (1880)) sodium acetate crystallizes from alcoholic solution in spear-formed needles and in plates.

[2] Determined in a capillary tube, with high-temperature mercury thermometer, in a bath of anthracene which had recently been distilled to make it transparent.

[3] Pogg. Ann., **102**, 293 (1857).

A warmed glass tube, constricted about ¼ inch above its lower end which was filled with a loose plug of absorbent cotton, served to remove a portion of the solution for analysis; the lower end of the tube was quickly cut off with a pair of scissors, and the solution blown out into a weighed crucible, which was immediately covered and weighed again. The water was driven off without spirting by heating for some hours in a steam bath at 95° and then to constant weight at 120°. The results are given in grams of anhydrous salt per 100 g water, and are in most cases the means of accordant determinations.

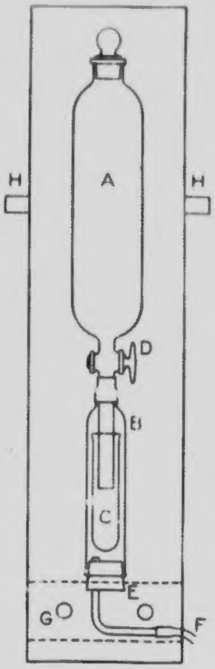

Fig. 2

At temperatures below 58°, where the solutions are supersaturated with respect to the trihydrate, the combination of tap funnel *A*, adapter *B*, and vial *C* shown in Fig. 2 was employed. A quantity of trihydrate was melted in the funnel, the apparatus set together and tied to the piece of board weighted at *G*, and was rocked about the axis *H* in a thermostat over night. A partial vacuum was then created in the adapter by means of a rubber tube attached to *F*, the tap *D* was opened a little and the vial filled. The tap was then closed and the whole removed from the thermostat; the stopper *E* and vial removed, part of the solution quickly poured into a crucible and treated as described. After washing and drying vial and adapter, the apparatus was ready for another determination.

Solubility of the Trihydrate.—These measurements were made in the open vessel used for the anhydrous salt above 58°; the results are expressed in the same units as before, *viz.*: grams of anhydrous salt to 100 grams of water in the solution. Four numbers are taken from Schiavon[1] and one from Guthrie.[2]

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[1] Gazz. Chim. Ital., **32**, 532 (1903)

[2] Phil. Mag. [5], 2, 215 (1876)

Table III gives the solubilities for every 10°, obtained by graphic interpolation from the figures of Table II. The data for the freezing-point and boiling-point curves are taken from tables by Legrand[1] and Guthrie,[2] respectively. The four curves in Fig. 3 give the compositions of solutions saturated with anhydride, trihydrate, ice, and steam at atmospheric pressure, respectively.

TABLE I

Expt.	Water Percent	Mols H_2O to one mol $C_2H_3O_2Na$	
	18.14	1.03	Zettnow's driest
a	33.0	2.24	Centrifuged
	5.4	0.3	Centrifuged
b	0.6	0.03	Drained hot
	0.37	0.016	Drained hot
	0.36	0.016	Drained hot
c	4.0	0.22	Bottom of funnel

TABLE II

Anhydrous				Trihydrate		
0°	119	72°.5	149	0°	36.2	Guthrie
25	125	83	154.3	9	40	Schiavon
34.8	129	83.5	154.3	13	43.5	Schiavon
43	131	100	170	37	61.0	Schiavon
50	133.5	123	193	41	68.0	Schiavon
61	140.5	—	—	51.5	87.5	Green
—	—	—	—	55.5	102	Green

TABLE III

Temp..........	-18°	-10°	0°	10°	20°	30°	40°	50°	58°
Ice..........	30.4	19.0	0	—	—	—	—	—	—
Hydrate........	30.4	33.0	36.3	40.8	46.5	54.5	65.5	83	138
Anhydrous.....	—	—	119	121	123.5	126	129.5	134	138

Temp..........	60°	70°	80°	90°	100°	110°	120°	123°
Anhydrous.....	139.5	146	153	161	170	180	191	193
Steam.........	—	—	—	—	0	69	156	193

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[1] Lieb. Ann., **17**, 36 (1836); see also Gerlach: Zeit. anal. Chem., **26**, 455 (1887).

[2] Loc. cit. See also Rüdorff: Pogg. Ann., **145**, 616 (1872).

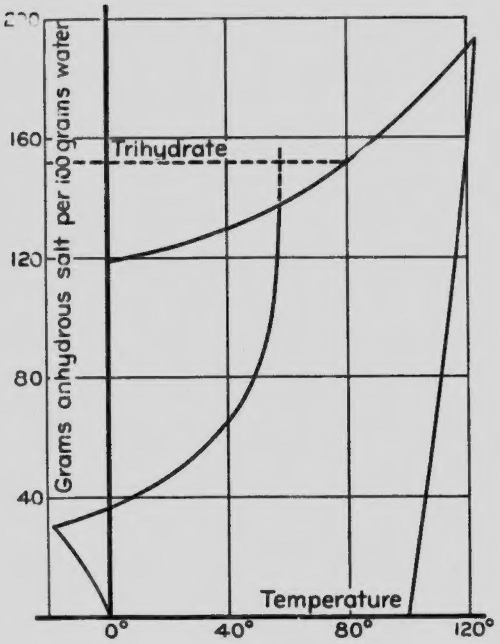

Fig. 3

Summary

The crystals deposited from supersaturated solutions of sodium acetate trihydrate have been isolated and analyzed; in confirmation of the results obtained by dilatometer measurements they consist of anhydrous sodium acetate. The crystalline form and the melting-point of the salt so obtained are those of ordinary anhydrous sodium acetate.

The solubility of the anhydrous salt has been determined from 0° to 123°—the boiling-point of the saturated solution; and that of the trihydrate from the cryohydratic point (Guthrie) to its "melting-point."

The "melting-point" of the trihydrate is a transition point, at which the reaction

$$C_2H_3O_2Na.3H_2O = 0.092\ C_2H_3O_2Na + \text{Sol'n}\ (0.908\ C_2H_3O_2Na + 3H_2O)$$

is in equilibrium. As noted by Jeannel, the "melting" at 58° is incomplete; the lowest temperature at which a clear solution can be obtained is obviously that at which the solution saturated with the anhydride has the same composition as the crystals of the trihydrate, *viz.*: 152 grams salt to 100 grams water. This is the case at 79°, where the dotted line corresponding to the composition of the trihydrate in Fig. 3 cuts the solubility curve of the anhydrous salt; Jeannel gives 75°, Zettnow 77° to 78°.

The "true melting-point," at which trihydrate is in equilibrium with a solution of its own composition, would be given by the intersection of the same dotted line with the solubility curve, produced, of the trihydrate. This temperature would be very little higher than that of the transition point, as at the true melting-point the tangent to the solubility curve must be perpendicular.

These measurements were carried out under the direction of Prof. W. Lash Miller in the chemical laboratory of the University of Toronto in the spring of 1903.

The University of Toronto
June, 1908.